FIRST QUARTERLY REPORT

STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION OF THE ALKALINE SILVER ELECTRODE

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ABSTRACT

1. A device has been constructed to permit the measurement and recording of the difference in potential (ΔE) at two points on a working silver electrode while simultaneously measuring the potential of the electrode relative to a reference electrode. Plots are presented which show how ΔE varies with the state of charge of the electrode and with current density.

2. Silver surfaces have been prepared both on glass and on silver foil by evaporation-deposition of silver. These surfaces show promise as the base for surface area estimation.

3. Gas chromatographic analysis of the products from pyrolysis of commercial sintered silver electrodes at temperatures up to 750°C indicates CO_2, CH_4, C_2H_4 and possibly other components. Infra-red analysis of the fractions verified the CH_4 and C_2H_4.

I. Potential Variations Over the Electrode Surface.

Apparatus and Reagents

A cell was designed and built with two Luggin capillaries mounted on micrometer drives to permit simultaneous measurement of potentials at the center and the edge of a working silver foil electrode. (See Fig. I)

The measuring circuit consisted of two separate mercury-mercuric oxide reference electrodes connected by the cell electrolyte (0.1 N KOH) through the two capillaries.

Because of the relatively high resistance in the measuring circuit a chopper, amplifier, oscilloscope system was used initially for null point detection. The reading with this system was reproducible to 0.02 mv. Later the potential difference was recorded on a Leeds and Northrup Speedomax H Continuously-Adjustable Azar Recorder. (Fig. I)..

The capillaries were made by drawing 3 mm soft glass tubing and then sealing Intramedic polyethylene tubing (O.D. .024", I.D. .011") into the constricted end with epoxy cement. The seal was tested for air tightness, water tightness, and electrical leakage. One of the tips was heated and bent to a 90° angle.

A silver foil electrode (99.9% 2.0 x 2.0 x 0.0011 cm) and a platinum foil electrode were used in the cell. The silver electrode was cleaned with cleansing powder and distilled water. This electrode was used for all the ΔE experiments reported here.

Two 90 volt batteries (Ray-O-Vac No. 204) in series with resistors of various sizes supplied the lower currents used. Currents above 8.0 ma were supplied by a Hewlett-Packard Model 881A X Power Supply on constant

current mode. The magnitude of each current was determined by measuring the voltage drop across a precision 1 ohm resistor with a Leeds and Northrup K-3 potentiometer.

Experiments and Results

With one capillary placed at the center and the other at the edge of a cleaned silver electrode, the potential difference was recorded during both oxidation and reduction. This measurement was repeated at current densities of 0.18, 0.36, 0.72, 1.44, 2.25 ma/cm^2. The curves obtained at the extreme and mid current values are shown in Fig. II. Since peaks in the ΔE curve seemed to correspond with changes in the state of oxidation of the electrode a Varian Recorder was placed across the silver electrode and a third mercury-mercuric oxide electrode to record the changing silver potential while the ΔE was simultaneously recorded on the L & N recorder. A close correlation was found between changes of potential on the silver electrode and potential differences from center to edge. (See Fig. II)

Discussion

Listed below are three possible models for explanation of the ΔE curves obtained.

1. A rate determining step involving migration of a silver or an oxygen species through the oxide layer.

   Dirkse[1] postulated that the mechanism for the Ag(I) oxidation included the migration of OH^- through the Ag_2O to the Ag_2O/Ag interface. The silver lattice, because of loss of electrons, was expanded and provided room for the inclusion

of O^{2-} from the OH^-. Barradas and Fraser[2] suggested that the rate determining step for the formation of AgO from Ag_2O was the transfer of O^{2-} ions at the Ag_2O/AgO interface. Others have considered mechanisms for electrolytic Ag oxidation based on the migration of Ag species.

2. Current density variations and differences in resistance over the electrode surface.

If a higher current density exists at the edges of a plane electrode as is postulated by Wagner[4] then the oxide layer at the edge should be thicker. This would result in a higher potential at the edge because of the greater iR drop. The high resistance of the thicker oxide film at the edge might eventually decrease the current flow there and limit the increase in potential difference. The formation of silver(II) oxide first at the edge would also cause a significant change in resistance over the plate since Cahan and co-workers[5] have reported that the resistance of Ag_2O is 10^5 times greater than of AgO.

3. Increased progression of the edge over the center along the potential time curve.

If two points separated by a fixed time are followed along the potential-time curve (See Fig. III) the difference in their potentials will depend upon the shape of the curve. At (a) in Fig. III points x and y have a potential difference of +230 mv while at point (b) they are at the same potential. At point (c) x - y = +20 mv and at point (d) x - y = -20 mv. If point x is the potential at the edge and point y is the potential

at the center, the change of x - y with time has some similarity to our graph of ΔE with time. The higher ΔE's at higher c.d. could be explained by assuming a greater time separation of the points x and y. This possibility will be tested by comparing the differential of the potential-time curve obtained by the use of an operational amplifier differentiation circuit with our ΔE curves.

A combination of these models may best explain the potential difference curves obtained.

Proposals for Further Work

We plan to determine the effect on the potential difference of the following variables:

1. Position of capillaries on the Ag electrode and distance of capillaries from the surface.
2. Electrode shape and composition.
3. Electrolyte composition and concentration.

Some exploratory experiments testing these effects have been done.

II. Surface Area Estimation

Depth of Oxidation

It is established that the depth of penetration of an oxide layer may be determined coulometrically by a measurement of the potential plateau length of that oxidation at constant current.[7] The following formula may be applied to the resulting data to find the depth of penetration expressed as the number of monolayers of penetration.

(1) $$x = \frac{N_o I T}{F\, a\left(\frac{P N_o}{M}\right)^{2/3}}$$

I = amps (constant current)

T = sec (length of plateau)

F = Faraday

a = cm^2 (surface area)

P = gm/cm^3 (density)

N_o = 6.02×10^{23}

M = gm/mole (molecular weight)

As one can see from equation (1) the surface area, a, must be known in order to determine the depth of penetration. We have attempted several methods to prepare a surface of known area. Another problem affecting the depth of penetration is the inherent irreproducibility of corrosion of metals.[8] This is caused primarily by grain and strain points created in the metal lattice during the working of these metals. In order to rid our surface of these imperfections we have prepared a silver surface by condensation of silver vapor onto a rigid support. The silver vapor is obtained by vacuum vaporization of silver from a

hot tungsten filament.[9] The rigid supports that have been tried are thin glass discs and polished silver foil. We have tried to prepare a layer of silver thick enough so that the oxidation reaction does not proceed completely through the layer of deposited silver.

The glass discs were used because of their smooth surfaces. The film formed by deposition of the evaporated silver will tend to follow the surface it is deposited upon.[9] Two problems have been encountered in this procedure. First, the non-conductive nature of glass requires one to make electrical contact on the metal surface. (See Fig. IV) Second, it may be that local heating occurs during oxidation because of the insulating property of the glass backing. Several electrodes prepared of silver on glass showed regions in which there was poor adhesion of the oxide during electrolytic reactions. For these reasons we have tried a second approach using silver foil as the rigid support.

The apparatus and techniques used in determining the plateau length for these oxidations is the same as that reported in the final report of J.P.L. 951157. Thus far results have not been much inside the 10% limit of workers who have used a similar technique for determination of depth of oxidation[7] (See Table I). It is hoped that improved polishing procedures and thicker silver films will overcome these problems.

Area Estimation

Once we have data for an electrode with a layer of silver of sufficient thickness for the oxidation reaction and whose surface is perfectly smooth, we can determine the depth of penetration as a

function of the current density,

$$x = \frac{it\ N_o}{a\ F\left(\frac{\rho N_o}{M}\right)^{2/3}}.$$

where a is not only the effective surface area but also the gross area of the electrode since it is perfectly smooth.

The assumption is then made that at a given current density the average depths of penetration will be the same for a very uneven surface as for the perfectly smooth surface. The effective surface area for an electrode with an irregular or uneven surface may then be calculated by collecting sufficient data to include a time representing the length of the plateau within the range of times for the smooth electrode.

The best approach to an electrode whose surface is perfectly smooth is represented by the series of silver electrodes plated on glass discs given in Table I.

Calculation using the data (area, 5.1 cm^2; time, 570 sec.; current 0.20 ma.) gives a depth of penetration

$$x = \frac{(2.0 \times 10^{-4})(570)}{(5.1)} \frac{(6.02 \times 10^{23})}{(96500)\left[\frac{(10.2)(6.02 \times 10^{23})}{(108)}\right]^{2/3}}$$

$$x = 92 \text{ monolayers}$$

for a current density 3.9×10^{-5} amp/cm^2.

The proposed work in this part of the project is

1. to collect additional data on depth of penetration vs current density with smooth electrodes.

2. calculation of surface areas of irregular surfaced silver electrodes.

3. correlation of these surface area measurements with measurements by other techniques[10].

III. Organic Residues in Sintered Silver Electrodes

Evidence was presented in the first quarterly report of J.P.L. Contract 951157 that commercial sintered silver electrodes may contain organic residues resulting from incomplete removal of organic binders during the sintering process.

The first part of an effort to determine the nature and amount of such residues in these electrodes involves the pyrolysis of samples of some Delco-Remy sintered silver electrodes and the examination of the products of pyrolysis by gas chromatography and infrared spectrophotometry.

Apparatus. A Perkin Elmer Vapor Fractometer Model 154 D with a Leeds and Northrup Speedomax G recorder was used for the gas chromatographic analyses. The infrared determinations were made with a Beckman IR 7 instrument. Two pyrolysis chambers were used and were connected directly into the path of the carrier gas to avoid loss of sample. The borosilicate pyrolysis chamber was fitted with a by-pass path so that the sample could be heated for five minutes in a tube furnace and then through a system of stopcocks swept into the main stream of carrier gas for analysis. The stainless steel tube was not fitted in this manner. The tube containing the sample was connected directly into the carrier gas path. The carrier passed through to sweep out the air present. Then the flow was stopped and the sample heated for five minutes. The flow of gas was then started and the analysis made.

Results and Discussion. The results of the gas chromatographic analyses are summarized in Tables II and III. The assignments in Table II where a silica gel column was used were made on the basis of gases we considered to be likely possibilities and comparison of the retention times of these with the retention times of the products of the pyrolyses. Oxygen, nitrogen and carbon dioxide, while their presence is indicated, may be merely adsorbed from the atmosphere. The presence of methane, ethane and ethylene is also indicated from their retention times. The presence of methane and ethylene was confirmed by the absorption of infrared radiation at particularly sensitive wave lengths. Even though the samples were very dilute in the helium carrier gas the run labeled III in Table II gave sufficient ethylene to be detected by an absorption at 949 cm^{-1} and methane to be detected by an absorption at 1300 cm^{-1}. Ethane and carbon dioxide have not been confirmed.

The data of Table III indicate the presence of water. The column used in this case was di-n-decylphthalate on firebrick.

A run was made in which the same sample was subjected to successive temperature increments: 100°C - 200° - 300° - 400° - 500°. Analysis was made after 5 minutes heating at each temperature. Of the ethylene that was evolved most came off the sample after the heating at 400°C.

Work will continue along the following lines:

1. Further effort to confirm carbon dioxide and ethane as products of pyrolysis.

2. Determination of products from pyrolysis in hydrogen.

3. Precise quantitative measurements of these components based on the electrode sample.

Table I

Reproducibility in Lengths of Oxidation Plateaus of Silver Electrodes

Type of Electrode	Length of Plateau	Deviation	Current
cleaned, unpolished	135 sec.	± 7%	0.3 ma
	140 sec.		
	150 sec.		
	155 sec.		
polished, cleaned, with detergent in ultrasonic cleaner	108 sec.	± 17%	0.3 ma
	105 sec.		
	93 sec.		
	126 sec.		
polished, cleaned, anodized 30 min, electroplated 2 hrs.	227 sec.	± 4%	0.3 ma
	223 sec.		
	219 sec.		
	220 sec.		
silver deposited on glass discs	600 sec.	± 4%	0.2 ma
	585 sec.		
	555 sec.		
	540 sec.		
silver deposited on silver foil	920 sec.	± 7%	0.2 ma
	840 sec.		
	1050 sec.		

Table II

Gas Chromatographic Analysis of Volatile Products From Pyrolyzed Sintered Silver Electrodes

Conditions: Silica Gel Column, 4 ft; Temperature of Column 28-34°C; Carrier Gas, Helium at 219 cm^3/min.

Sample and Weight	Temperature of Pyrolysis	Analytical Data				
		Specific Peak	Retention Time	Peak Area Relative	Assignment	Weight % of solid Sample
I. Delco-Remy Sintered Electrode ~1.0 g.	500° (in borosilicate pyrolysis chamber)	1	1.3 min.	7	---	---
		2	1.7 min.	89	N_2, O_2, CH_4	1.1×10^{-3}
		3	5.6	9	C_2H_6	4.4×10^{-4}
		4	7.2	70	CO_2	5.9×10^{-3}
		5	9.4	50	C_2H_4	1.7×10^{-3}
II. Delco-Remy Sintered Electrode 7.7092 g.	500° (in borosilicate pyrolysis chamber)	1	1.75	1540	N_2, O_2, CH_4	
		2	5.3	4	C_2H_6	
		3	7.0	2320	CO_2	
		4	8.9	192	C_2H_4	
Standards						
Ethane			5.6			
Carbon Dioxide			7.1			
Ethylene			9.3 (ave.)			
Methane			1.3			

Table II (Continued)

Sample and Weight	Temperature of Pyrolysis	Analytical Data: Specific Peak	Retention Time	Peak Area Relative	Assignment	% Weight of solid Sample
III. Delco-Remy Sintered Electrode ~1.0 g.	750° (in stainless steel tube)	1	.6	---	N_2, O_2	
		2	.8	---	CH_4	
		3	1.5	---	---	
		4	3.95	4	C_2H_6	6.0×10^{-5}
		5	5.1	100	CO_2	2.1×10^{-3}
		6	6.65	36	C_2H_4	4.9×10^{-4}
Standards	(in stainless steel tube)					
Ethane (.31 mg)			3.9	1940		
Carbon Dioxide (.43 mg)			5.7	1870		
Ethylene (.19 mg)			7.8	1536		

Table III

Gas Chromatographic Analysis of Volatile Products from Pyrolyzed Sintered Silver Electrodes.

Conditions: n-decyl phthalate column, 3 feet; temperature of column 100°C carrier gas helium at 135 cm^3/min.

Sample and Weight	Temperature	Analytical Data				
		Specific Peak	Retention Time	Peak Area Relative	Assignment	% Weight
I. Delco-Reny Sintered Electrodes 1.1056 g.	250° (in glass apparatus)	1	1.25	---	---	
		2	2.0	71	Gases	
		3	5.8	304	H_2O	.023%
	500°	1	1.4	Small	---	
		2	1.9	66	Gases	
		3	8.1	248	H_2O	.014%
$CuSO_4 \cdot 5\ H_2O$ .0009 g.	250°	1	4.5	865	H_2O	

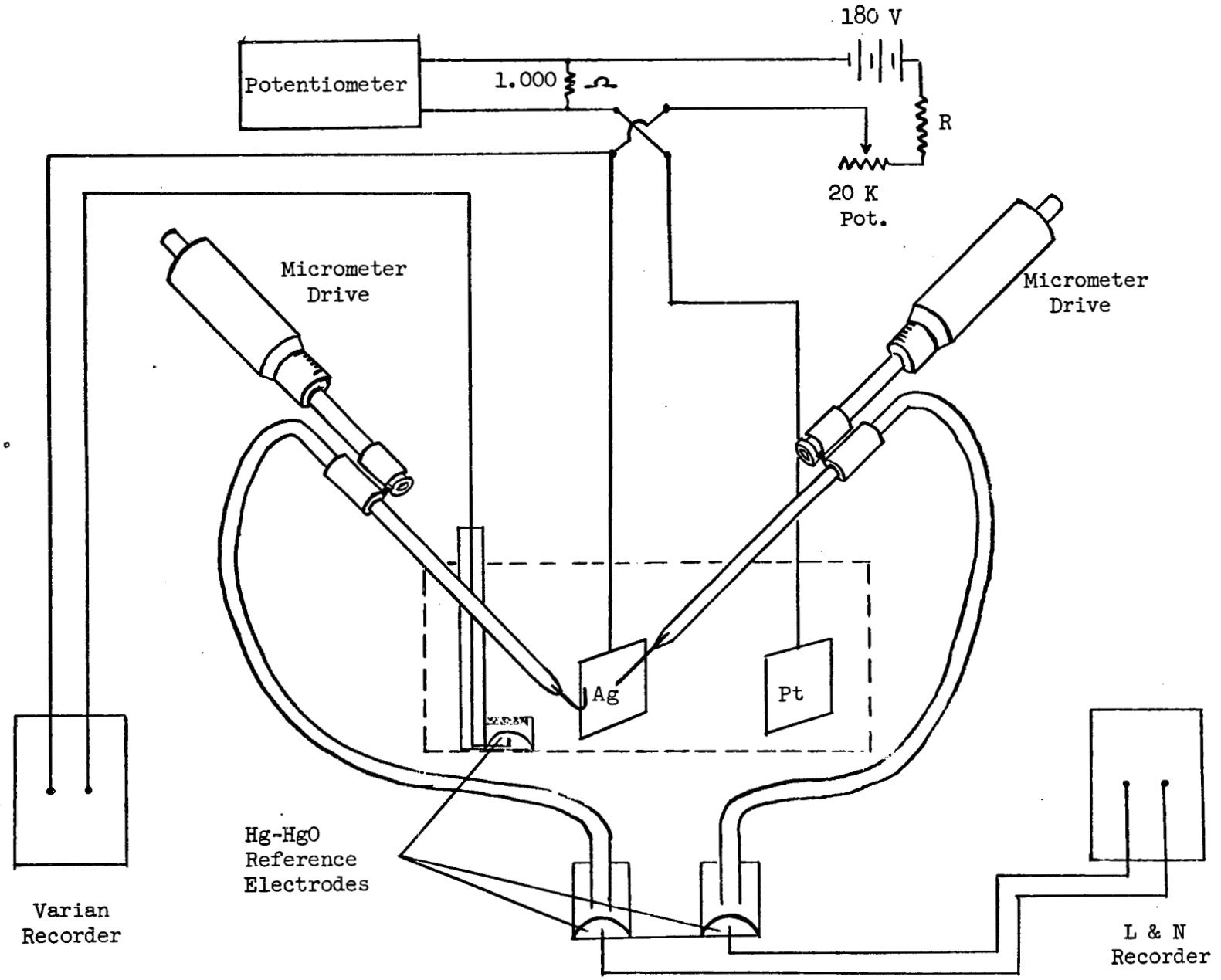


Figure I

Block diagram of test cell and electrical circuit

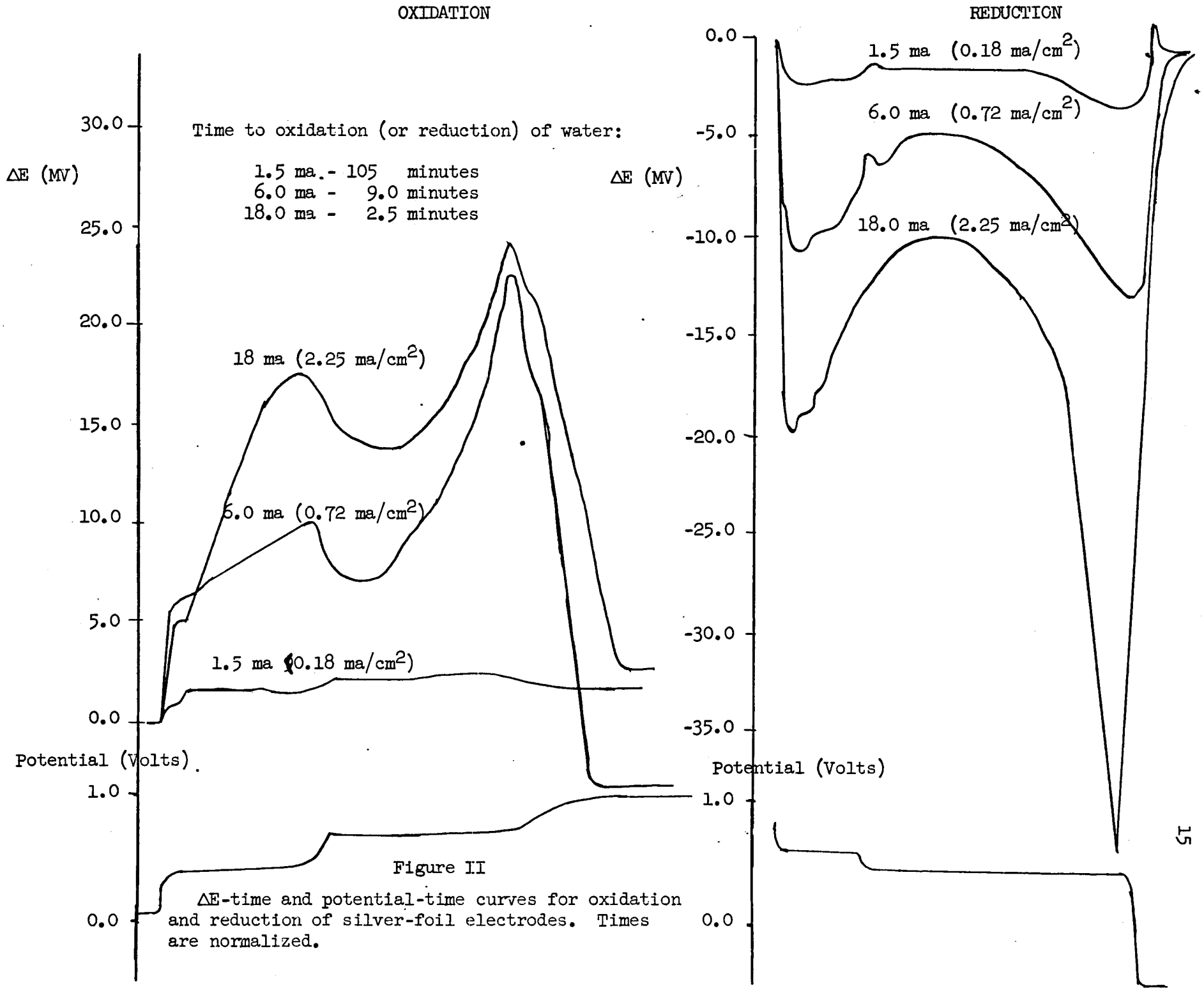


Figure II

ΔE-time and potential-time curves for oxidation and reduction of silver-foil electrodes. Times are normalized.

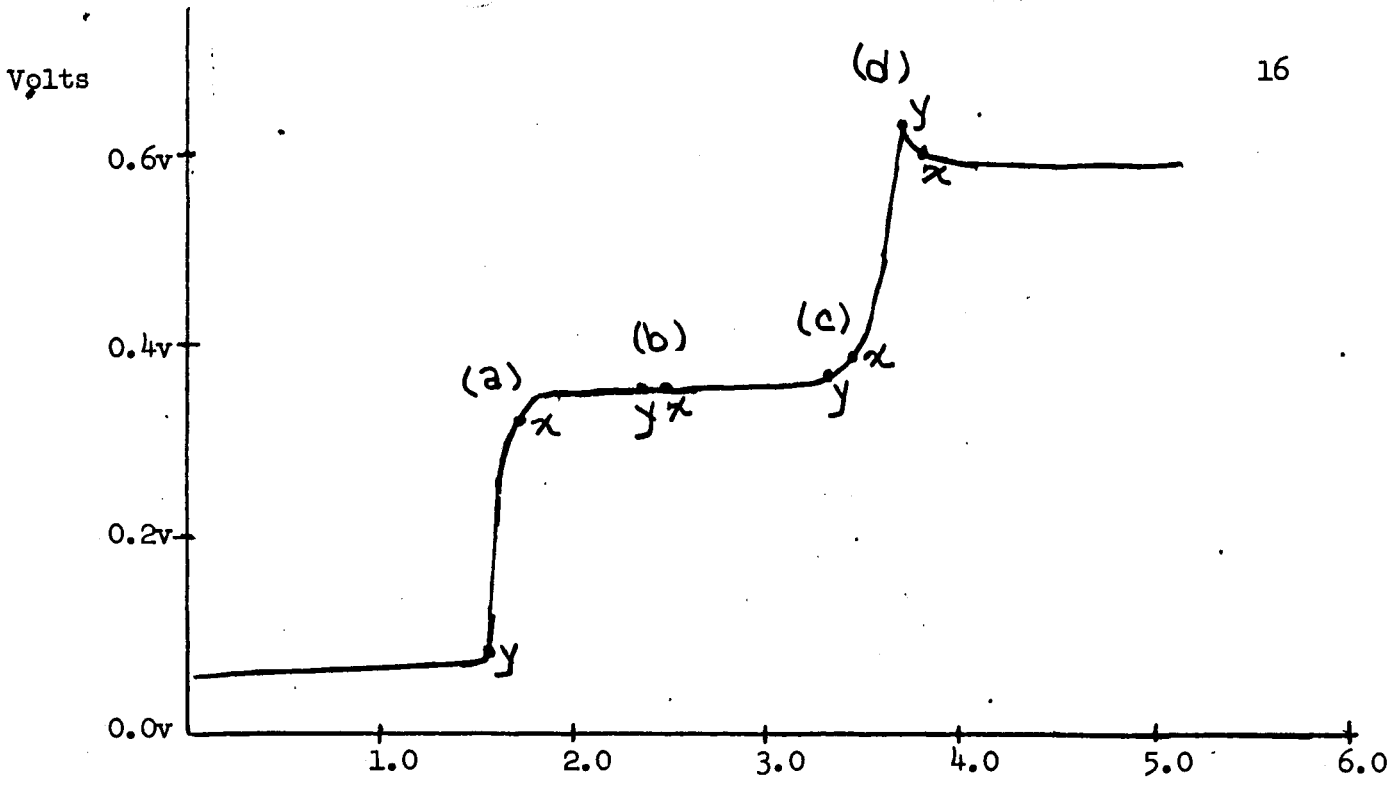
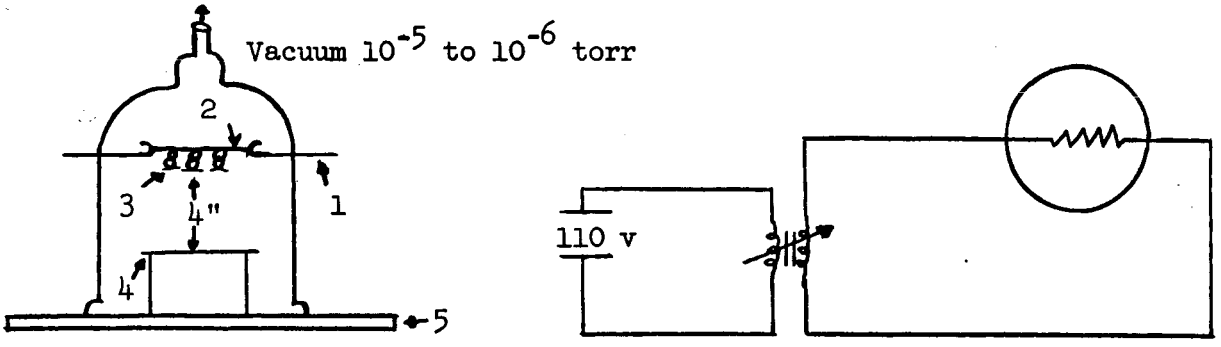


Figure III

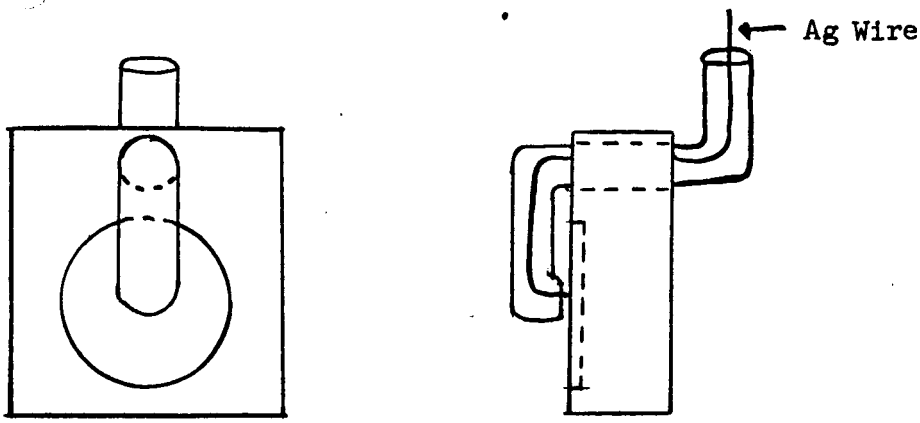
Typical Potential Time Curve During Oxidation of Silver



1. Thick tungsten wire used for leads
2. 32 gauge tungsten wire wound around 4 mm glass rod for heating coil
3. Silver wire loops (.020" - 1/8" long)
4. Glass plate for support of objects to be coated
5. 1/8" ground pyrex plate, sealed with high vacuum grease

Figure IV

Vacuum Vaporization Apparatus



The holder is made of teflon which has a milled recess to hold glass discs. A glass tube fitted with a sealed silver wire is used to make contact with silver surface.

Figure V

Glass-Disc Holder

BIBLIOGRAPHY

1. Dirkse, T. P., J. Electrochem. Soc., 106, 920-25 (1959).

2. Barradas, R. G. and Fraser, G. H., Can. J. Chem., 42 (II), 2488-95 (1964).

3. Knoz, L. L., Teikis, D. I., Vidovitsh, G. L., and Kabanov, B. N., Z. Physik. Chem. Leipzig, A, 214, 334 (1960).

   Göhr, H. and Lange, E., Z. Physik. Chem. Frankfurt, 17, 100 (1958).

4. Wagner, C., J. Electrochem. Soc., 98, 116-128 (1951).

5. Cahan, B. D., Ockerman, J. B., Amlie, R. F., and Ruetschi, P., J. Electrochem. Soc., 107, 725-31 (1960).

6. Berrard, J., "L'Oxydation des Metaux," pp. 97 ff, Gauthier-Villars et Cie, Paris (1962).

7. Allen, J. A., Trans. Faraday Soc., 48, 273 (1952).

8. Evans, U. R., "The Corrosion and Oxidation of Metals," Chapt. XXII, Edward Arnold Ltd., London (1960).

9. Olsen, L. O., Smith, C. S., Crittenden, E. C., Jr., J. App. Phys., 16, 425-33 (1945).

10. McCallum, J., Walling, J. F., and Faust, C. C., "Measurement of True Surface Area in Electrodes," First Quarterly Technical Progress Report, Battelle Memorial Institute, Columbus, Ohio (Undated).